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**(54) INJECTION MATERIAL FOR LOWERING HEXAVALENT CHROMIUM**

**(57)Abstract:**

PROBLEM TO BE SOLVED: To provide an injection material for lowering hexavalent chromium, which enables the reduction of a dissolution amount of hexavalent chromium, excels in permeability and reduces the dissolution of hexavalent chromium included in a fine grain cement that is excellent in an appearance of strength.

SOLUTION: The injection material for lowering hexavalent chromium includes the fine grain cement, a fine grain slag, calcium aluminate and gypsum, and furthermore, is comprised of including a reducing agent.

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CLAIMS

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[Claim(s)]

[Claim 1] Particle cement, particle slag, calcium aluminate, and a low hexavalent chromium injecting material containing gypsum fibrosum.

[Claim 2] The low hexavalent chromium injecting material containing a reducing agent according to claim 1.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the low hexavalent chromium injecting material which reduces elution of the hexavalent chromium which particle cement contains. The part of this invention and % are mass bases as long as there is no regulation especially.

[0002]

[Description of the Prior Art] Now, the injecting material currently used in the civil-engineering-and-construction field is divided roughly into a water glass system injecting material and a cement system injecting material. Although the perviousness of a water glass system injecting material is good compared with a cement system injecting material, SUBJECT that endurance is bad occurs. Even if a water glass system injecting material is used for a silt layer, a clay stratum, etc., as for perviousness, they serve as what is called a fracture grouting form to which a water glass system injecting material enters a silt layer and a clay stratum by fluid pressure at a wedge shape undesirably. However, since a water glass system injecting material had the small compressive strength (gay gel strength) of itself, there was a case where reinforcement or the stop effect of the foundation were not acquired.

[0003] Then, a cement particle is atomized, the injecting material which improved the perviousness of the cement system injecting material is developed, and reinforcement and the stop effect of the foundation came to be acquired by atomization of cement also in the silt layer or the clay stratum in recent years.

[0004] On the other hand, processing of various kinds of industrial waste is expected from the cement industry.

Using industrial waste, such as a sewage sludge and an old tire, for manufacture of cement is performed, and it is expected that the amount used continues to increase.

In connection with it, we are anxious about the detrimental constituent contained with cement, and hexavalent chromium content increasing especially.

[0005] Then, since hexavalent chromium is fixed, the method of adding blast furnace slag or adding ferrous sulfate is examined (JP,2000-086322,A). However, since [ that specific surface area will increase and the amount of hexavalent chromium to elute will increase if cement is atomized in order to raise perviousness by this method, since the time to hardening is still as longer as several hours ], It has not been improved by that hexavalent chromium is spread from groundwater etc. before hardening etc., but it had SUBJECT that sufficient effect was not acquired.

[0006] When particle cement is used, by using a specific material, this invention person acquires the knowledge that the elution volume of hexavalent chromium can be reduced, and came to complete this invention.

[0007]

[Means for solving problem] That is, this inventions are particle cement, particle slag, calcium aluminate, and a low hexavalent chromium injecting material containing gypsum fibrosum.

It is this low hexavalent chromium injecting material containing a reducing agent.

[0008]

[Mode for carrying out the invention] Hereafter, this invention is explained in detail.

[0009] What usually atomized various portland cement, such as high-early-strength and super-high-early-strength one, as particle cement used by this invention, And the cement etc. which mixed fly ash, limestone, or silicon sand atomized by specific surface area of cement by blaine more than 5 and 000cm<sup>2</sup>/g, for example are mentioned to the these-atomized portland cement. 5 and more than 000cm<sup>2</sup>/g of the particle size of particle cement are preferred at specific surface area of cement by blaine, 8 and more than 000cm<sup>2</sup>/g are more preferred, and 12 and more than 000cm<sup>2</sup>/g are the most preferred. Perviousness may worsen by 5 and less than 000cm<sup>2</sup>/g.

[0010] As for the particle slag used by this invention, although blast furnace slag, converter slag, etc. are atomized, what atomized the amorphous substance which quenched blast furnace slag among these is preferred from the field of intensity manifestation nature. 5 and more than 000cm<sup>2</sup>/g of the particle size of particle slag are preferred at specific surface area of cement by blaine, 8 and more than 000cm<sup>2</sup>/g are more preferred, and 12 and more than 000cm<sup>2</sup>/g are the most preferred. Perviousness may worsen by 5 and less than 000cm<sup>2</sup>/g. As for the amount of the particle slag used, 50-1,000 copies are preferred to 100 copies of particle cement, and its 200-500 copies are more preferred. If it is less than 50 copies, the fixed rate of hexavalent chromium may become small, and if it exceeds 1,000 copies, early age strength may fall.

[0011] With the calcium aluminate used by this invention. . Mix the raw material containing calcia and the raw material containing alumina, and are obtained by heat-treating calcination with a kiln, melting in an electric furnace, etc. It is the general term of the substance which has hydration activity which used CaO and Al<sub>2</sub>O<sub>3</sub> as the main ingredient, A part of CaO and/or Al<sub>2</sub>O<sub>3</sub> An alkali metal oxide, It is the substance in which these dissolved to the compound replaced by an alkali earth metal oxide, alkali metal halides, alkaline earth metal halide, alkali metal sulfate, alkaline-earth-metals sulfate, etc., or the thing which uses CaO and Al<sub>2</sub>O<sub>3</sub> as the main ingredients. as a mineral form -- a crystalline substance -- amorphous -- they may be any. In these, amorphous calcium aluminate is preferred in respect of labile, and the amorphous calcium aluminate which quenched the thermally treated material corresponding to 12CaO and a 7Al<sub>2</sub>O<sub>3</sub> (C12A7) presentation is more preferred. 5 and more than 000cm<sup>2</sup>/g of the particle size of calcium aluminate are preferred at specific surface area of cement by blaine, and 8 and more than 000cm<sup>2</sup>/g are more preferred. Perviousness may worsen by 5 and less than 000cm<sup>2</sup>/g. As for the amount of the calcium aluminate used, 1-200 copies are preferred to 100 copies of particle cement, and its 10-50 copies are more preferred. In less than one copy, there is a possibility that the fixed rate of hexavalent chromium may become small, and even if it exceeds 200 copies, improvement is not expectable from that of the fixed rate of hexavalent chromium.

[0012] As gypsum fibrosum used by this invention, anhydrous gypsum, hemihydrate gypsum, gypsum dihydrate, etc. are mentioned, and chemical gypsum, such as further natural gypsum fibrosum, phosphoric acid gypsum fibrosum, flue-gas gypsum, fluoric acid gypsum fibrosum, or the gypsum fibrosum produced by heat-treating these is mentioned. In these, anhydrous gypsum is preferred in respect of intensity manifestation nature being large. 5 and more than 000cm<sup>2</sup>/g of the particle size of gypsum fibrosum are preferred at specific surface area of cement by blaine, and 8 and more than 000cm<sup>2</sup>/g are more preferred. Perviousness

may worsen by 5 and less than 000cm<sup>2</sup>/g. As for the amount of the gypsum fibrosum used, 0.1-100 copies are preferred to 100 copies of particle cement, and its 1-30 copies are more preferred. In less than 0.1 copy, if early-age-strength manifestation nature may become small and exceeds 100 copies, the fixed rate of hexavalent chromium may become small.

[0013]Iron salt divalent [ as a reducing agent used by this invention /, such as iron(II) sulfate, ], Sulfate, such as trivalent titanium salt, such as titanium sulfate (III), sodium sulfite, Hydrogensulfites, such as sulfite salt, such as potassium sulfite and calcium sulfite, sodium hydrogen sulfite, and potassium bisulphite, Sulfides, such as a sodium sulfide, a potassium sulfide, calcium sulfide, and ammonium sulfide, There are thiosulfate salt, such as sodium subsulfite and potassium thiosulfate, sulfur dioxide and sulfur, peat, brown coal, etc., and the field where the fixed rate of hexavalent chromium is large to use of iron(II) sulfate, sodium subsulfite, or potassium thiosulfate is [ among these ] preferred at small-quantity use. As for the amount of the reducing agent used, 0.01-50 copies are preferred to 100 copies of particle cement, and its 0.1-5 copies are more preferred. If it is less than 0.01 copy, the fixed rate of hexavalent chromium may become small, and even if it adds exceeding 50 copies, the fixed rate of hexavalent chromium may not change.

[0014]In order to adjust so that the cure time to need may be acquired in this invention, it is preferred to use a setting modifier together. As a setting modifier, specifically Aluminates, such as sodium aluminate and potassium aluminate, Carbonate, such as sodium carbonate and potassium carbonate, sodium hydroxide, a potassium hydrate, Hydroxide, such as calcium hydroxide and magnesium hydroxide, aluminum sulfate, Sulfate, such as iron(III) sulfate and alum, a sodium silicate, Silicofluorides, such as silicates, such as a potassium silicate and a lithium silicate, sodium silicofluoride, and magnesium hexafluosilicate, Phosphates, such as sodium phosphate, calcium phosphate, and magnesium phosphate, Organic acid, such as mineral, such as borate salt, such as lithium borate and sodium borate, citrate, gluconic acid, tartaric acid, and malic acid, or the sodium salt of those, potassium salt, lithium salt, calcium salt, sugars, etc. are mentioned. In particular since the amount of the setting modifier used adjusts according to cure time, it is not limited, but its 0.01-50 copies are preferred to 100 copies of particle cement.

[0015]In order to raise perviousness, it is preferred to use a dispersing agent together. As a dispersing agent, the dispersing agent of a formalin-condensation-product-salt-of-naphthalenesulfonic-acid system, a ligninsulfonic acid salt system, a melamine sulfonic acid formalin condensate salt system, a polycarboxylate system, and a polyether system is preferred. As for the amount of the dispersing agent used, 0.01-10 copies are preferred to 100 copies of particle cement, and its 0.1-3 copies are more preferred. In less than 0.01 copy, if perviousness may be inferior and it exceeds ten copies, early age strength may fall.

[0016]A reducing agent is contained further if needed, water is mixed [ particle cement, particle slag, calcium aluminate and gypsum fibrosum and ] with this injecting material, it is considered as suspension, and the low hexavalent chromium injecting material (henceforth this injecting material) of this invention can be poured into the foundation etc. Although the amount of this injecting material used changes with the kind of target soil, water content, the intensity to need, etc. and is not determined uniformly, its 5-300 kg is preferred to soil 1m<sup>3</sup>, and, generally, its 50-150 kg is more preferred. In less than 5 kg, hardened strength may be small, and if it exceeds 300 kg, hardened strength may become large too much.

[0017]The amount of water in the case of using this injecting material as suspension will not be limited especially if suspension is the viscosity which can be fed with a pump. For example, 100-1,000 copies are preferred to a total of 100 copies of particle cement, particle slag, calcium aluminate, gypsum fibrosum, and a reducing agent, and 200-500 copies are more preferred. In less than 100 copies, if viscosity may become high too much and exceeds 1,000 copies, hardened

strength may fall.

[0018]When mixing this injecting material with water and considering it as suspension, it may pour into the foundation by what is called one shot that blends a reducing agent with them further, is mixed by a mixer particle cement, particle slag, calcium aluminate, gypsum fibrosum and water, and if needed, and is poured in with a pump. In this case, since this injecting material may harden with a mixer, a pump, a hose, etc., it is necessary to secure cure time at least 30 minutes or more. Then, the suspension which consists of particle cement, particle slag, and water, for example, Calcium aluminate, gypsum fibrosum, and the suspension that consists of reducing agents are prepared independently, It is more preferred that what is called an injection method of 1.5 shots that mixes and pours in two kinds of suspension by a Y tube pours into the foundation by what is called two shots that feed the two above-mentioned kinds of suspension independently, and mix and pour it in at the tip of the double pipe for pouring again.

[0019]To this injecting material, bentonite, an allophane, methyl cellulose, It is also possible to use together defoaming agents, such as cellular agents, such as segregation resistance material, such as hydroxyethyl cellulose, hydroxyethyl methyl cellulose, and polyvinyl alcohol, gelatin, casein, and metallic aluminum, and paraffin, and silicone, etc.

[0020]This injecting material can be used for grouting used now, such as a mono tube rod construction method, a mono tube strainer construction method, a double pipe single phase construction method, a double pipe diplophase construction method, and a double pipe double packer construction method.

[0021]

[Working example]Although the example of an experiment of this invention is shown and this invention is explained further hereafter, this invention is not limited to these.

[0022]The particle slag, calcium aluminate, and gypsum fibrosum which are shown in Table 1 were mixed to 100 copies of example of experiment 1 particle cement, and this injecting material was prepared. 100 copies of these injecting materials and 300 copies of water which were prepared were mixed, suspension was produced, and the cure time, the compressive strength, and the hexavalent chromium elution volume of this injecting material were measured. A result is written together to Table 1.

[0023]<Material-of-construction> particle cement : An ordinary-portland-cement pulverizing article, The specific surface area of cement by blaine 12, 500cm<sup>2</sup>/g particle slag: A quenching blast-furnace-slag pulverizing article, the specific surface area of cement by blaine 13, the glass of a 000cm<sup>2</sup>/g calcium aluminate:C12A7 presentation, the specific surface area of cement by blaine 8, 500cm<sup>2</sup>/g.

Gypsum fibrosum : natural anhydrous gypsum, the specific surface area of cement by blaine 9, 000cm<sup>2</sup>/g [0024]<Test-method> cure time : Time compression intensity even if suspension is put into a cup and it concentrates, until suspension will not flow : According to JIS R 5201, it applies to measurement, and measurement age one day, and the 28-day hexavalent chromium elution volume:Environment-Protection-Agency notification No. 46 correspondingly, and they are measurement, measurement age one day, and 28 days. [0025]

[Table 1]

実験 No.	微粒子 スラグ	カルシウム アルミ ネート	石膏	硬化 時間 (分)	圧 縮 強 度		6 価 $\text{Cr}^{6+}$ 溶 出 量		備 考
					1 日	28 日	1 日	28 日	
1- 1	0	20	20	0.5	0.8	1.8	9.20	0.22	比較例
1- 2	50	20	20	0.8	0.7	2.0	3.13	N.D.	実施例
1- 3	100	20	20	1	0.6	2.2	1.09	N.D.	実施例
1- 4	200	20	20	2	0.5	2.4	0.61	N.D.	実施例
1- 5	400	20	20	4	0.3	2.4	0.20	N.D.	実施例
1- 6	500	20	20	6	0.2	2.5	0.10	N.D.	実施例
1- 7	1000	20	20	8	0.1	2.7	0.05	N.D.	実施例
1- 8	400	0	20	* 1	—	1.6	12.42	0.36	比較例
1- 9	400	1	20	25	0.1	1.8	4.29	N.D.	実施例
1-10	400	10	20	6	0.2	2.2	0.34	N.D.	実施例
1- 5	400	20	20	4	0.3	2.4	0.20	N.D.	実施例
1-11	400	50	20	2	0.6	2.6	0.17	N.D.	実施例
1-12	400	100	20	1	0.8	2.7	0.10	N.D.	実施例
1-13	500	200	20	0.5	1.1	2.8	0.05	N.D.	実施例
1-14	400	20	0	2	0.08	1.7	0.34	N.D.	比較例
1-15	400	20	0.1	2	0.15	1.9	0.30	N.D.	実施例
1-16	400	20	1	3	0.2	2.0	0.21	N.D.	実施例
1-17	400	20	10	4	0.3	2.3	0.15	N.D.	実施例
1- 5	400	20	20	4	0.3	2.4	0.20	N.D.	実施例
1-18	400	20	30	5	0.4	2.5	0.24	N.D.	実施例
1-19	400	20	100	7	0.5	2.6	0.31	N.D.	実施例

微粒子スラグ、カルシウムアルミネート、及び石膏は微粒子セメント100部に対する(部)、硬化時間の\*1は1日以上、圧縮強度は(N/mm<sup>2</sup>)で、—は未硬化、6価 $\text{Cr}^{6+}$ 溶出量は(ppm)でN.D.は定量限界値0.05ppm未満

[0026] It carried out like the example 1 of an experiment except having mixed 400 copies of particle slag, 20 copies of calcium aluminate, 20 copies of gypsum fibrosum, and the reducing agent shown in Table 2 to 100 copies of example of experiment 2 particle cement, and having produced this injecting material. A result is written together to Table 2.

[0027] <Material-of-construction> reducing agent a : Iron(II) sulfate, commercial item reducing agent b : Sodium sulfite, Commercial item reducing agent c : Sodium hydrogen sulfite, commercial item reducing agent d : A sodium sulfide, commercial item reducing agent e : Sodium subsulfite, commercial item reducing agent f : Potassium thiosulfate, commercial item reducing agent g : Sulfur, commercial item

[0028]

[Table 2]

実験 No.	還元剤	硬化 時間 (分)	圧 縮 強 度		6 価クロム溶出量		備 考
			1 日	28日	1 日	28 日	
1- 5	— 0	4	0.3	2.4	0.20	N. D.	実施例
2- 1	a 2	3	0.4	2.5	N. D.	N. D.	実施例
2- 2	b 2	5	0.2	2.3	0.11	N. D.	実施例
2- 3	c 2	5	0.2	2.3	0.10	N. D.	実施例
2- 4	d 2	4	0.3	2.4	0.09	N. D.	実施例
2- 5	e 2	3	0.3	2.3	N. D.	N. D.	実施例
2- 6	f 2	3	0.4	2.4	N. D.	N. D.	実施例
2- 7	g 2	5	0.2	2.3	0.10	N. D.	実施例
2- 8	a 0.01	4	0.3	2.4	0.15	N. D.	実施例
2- 9	a 0.1	4	0.3	2.4	0.11	N. D.	実施例
2-10	a 1.0	3	0.4	2.5	0.08	N. D.	実施例
2- 1	a 2	3	0.4	2.5	N. D.	N. D.	実施例
2-11	a 5	2	0.5	2.4	N. D.	N. D.	実施例
2-11	a 10	1	0.6	2.3	N. D.	N. D.	実施例
2-12	a 50	0.5	0.7	2.1	N. D.	N. D.	実施例

還元剤は微粒子セメント100部に対する(部)、圧縮強度は(N/mm<sup>2</sup>)で、6 価クロム溶出量は(ppm)でN. D. は定置限界値0.06ppm未満

[0029]The No. 7 silica sand was put into the polyethylene tube with a 5 example of experiment 3 cm[ in diameter ] x length of 30 cm until it was set to 20 cm in height. On the other hand, 400 copies of particle slag, 20 copies of calcium aluminate, 20 copies of gypsum fibrosum, one copy of setting modifier shown in Table 3, and one copy of polyether system dispersing agent were mixed to 100 copies of particle cement, and this injecting material was produced. 300 copies of water was mixed with 100 copies of these injecting materials, suspension was produced, this suspension was calmly thrown into the polyethylene tube into which sand was put, and the osmosis length, the compressive strength, and the hexavalent chromium elution volume to sand were measured. A result is written together to Table 3.

[0030]<Material-of-construction> setting modifier A: Sodium silicofluoride, reagent setting modifier B:citrate, the reagent setting modifier C:sodium tartrate, reagent setting modifier D:malic acid, reagent dispersing agent : Powder type commercial item [0031]The osmosis length to <measuring-method> sand: The cured body was taken out from the polyethylene tube one day afterward, and the length of the cured body was made into osmosis length. [0032]

[Table 3]

実験 No.	凝結 調整剤	硬化 時間 (分)	圧 縮 強 度		6 価クロム溶出量		砂への 浸透 長さ	備 考
			1 日	28日	1 日	28 日		
3- 1	—	4	0.4	2.6	N. D.	N. D.	10	実施例
3- 2	A	15	0.5	2.7	N. D.	N. D.	18	実施例
3- 3	B	45	0.5	2.8	N. D.	N. D.	20	実施例
3- 4	C	65	0.4	2.6	N. D.	N. D.	20	実施例
3- 5	D	60	0.5	2.7	N. D.	N. D.	20	実施例

凝結調整剤は微粒子セメント100部に対する(部)、圧縮強度は(N/mm<sup>2</sup>)で、6 価クロム溶出量は(ppm)でN. D. は定置限界値0.05 ppm未満、砂への浸透長さは(cm)

[0033]

[Effect of the Invention]As mentioned above, the elution volume of (1) hexavalent chromium can be reduced by using the low hexavalent chromium injecting material of this invention.

(2) Excel in perviousness.

(3) Excel in strong manifestation nature.

The effect of \*\* is done so.